Phase Transitions and Soft Modes

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(Received 2 August 1971; revised manuscript received 21 December 1971)

The stability of an equilibrium phase is described in thermodynamics in terms of certain convexity properties of the free energy. The phase is said to be unstable with respect to an equilibrium phase transition if the isothermal response of the system to a static external field is infinite. It is also known that associated with several second-order and some first-order transitions there are "soft collective modes" (for instance, in ferroelectric, antiferromagnetic, liquid-gas, and structural phase transitions). In this paper we show that in systems where the order parameter can be treated as an ergodic variable, and which possess collective excitations, at least one of the collective modes must go soft when the system undergoes a second-order phase change (or more generally, at the stability limit of the system). Implications to discontinuous first-order transitions are also briefly discussed. Examples of soft modes associated with phase changes are given.

I. INTRODUCTION

An equilibrium state of a system consists of one or more macroscopically homogeneous regions—called *phases*. These equilibrium states can be described by thermodynamics, and can be parametrized by a finite number of thermodynamic parameters which determine all the thermodynamic functions. It is believed that thermodynamic functions depend piecewise analytically on the parameters; the singularity corresponds to changes in the phase structure of the system or in other words "phase transitions." The characterization of these singularities is believed to be the central problem in the theoretical understanding of phase transitions. The change of phase of a system usually involves a "symmetry breaking." In the liquid-solid transition, for example, the continuous translational symmetry is broken. The precise symmetry which is broken is sometimes more subtle. In order to characterize this symmetry breaking Landau introduced the concept of an order parameter ψ.[1] The order parameter is defined in such a way that it has nonzero positive or negative value in the less symmetrical (or low-temperature) phase and is zero in the symmetrical (or high-temperature) phase. In continuous phase transitions the suitably defined order parameter vanishes continuously as one approaches the transition temperature from below. In discontinuous transitions there is a discontinuous jump in the order parameter to zero at the transition temperature. Examples of order parameters are the spontaneous magnetization vector of an isotropic ferromagnet, the mean value of the rotation angle of the BO_6 octahedra in structural phase transitions in perovskite-type crystals,[2] the density difference $(\rho_L - \rho_G)$ in the condensation of gas, etc.

A state in thermodynamic equilibrium corresponds to a state of maximum entropy and of a minimum free energy. To be more specific, for an equilibrium phase (i) with all other parameters fixed, the free energy must be a convex upwards function of the temperature, and (ii) with all other thermodynamic parameters fixed, the free energy is required to be a convex downward function of the order parameter—in fact, this condition determines the other parameter for the equilibrium phase.[3] These general thermodynamic principles correspond to a requirement of the positivity of the heat capacity and the isothermal susceptibility (which is the static response of the system to an external field). An infinite response indicates that an equilibrium state is not a stable state. In this connection one singles out the response of the system to a field that couples to the order parameter. This is done because it is believed that the response to such a field exhibits the most singular behavior at the stability limit. Alternatively, one may use this as a criterion for the choice of the order parameter. Examples of such fields that couple to the order parameter are uniform magnetic field for a ferromagnet, or a "staggered" field for an antiferromagnet. It should be remarked upon that such "ordering fields" are not always physically realizable.

One may also study the stability of a many-body system differently. We can examine the dynamical response of the system to an infinitesimal time-dependent field. It is well known that the dynamical response is related to the excitation spectrum of the many-body system.[4] We can then discuss the stability of the system in terms of the stability of these excitations. The particular excitation which becomes unstable, as the system approaches the stability limit, is called a "soft mode" or "critical mode"—there may be more than one of these. More precisely, the system becomes unstable against the excitation of these modes. Examples of these are well known,[5] for instance, at the ferroelectric phase transitions,[6] the paramagnetic-anti-

ferromagnetic transitions,[7] several (second-order) structural phase transitions,[8–10] the liquid–gas phase transition, and the λ transition of ^{4}He.[10]

In this paper we attempt to unify the two above-mentioned points of view. More specifically, we show that in realistic systems (with dynamics), associated with all second-order phase transitions there must be at least one soft mode.

In Sec. II we discuss in detail the stability of an equilibrium state against an infinitesimal stationary perturbation that couples to the order parameter of the phase. It is demonstrated that at the limit of stability the static response function diverges.

In Sec. III we study the dynamical response of the system to a time-dependent external field. We show, following Kubo, that the zero-frequency Fourier component of the dynamical response function is equal to the static response function discussed in Sec. II. Such a step involves assuming that the order parameter is an ergodic variable. We then show that at the stability limit at least one of the collective excitations of the system must go "soft." That is, the complex frequency of that critical mode tends to zero. Since it is well known that for certain modes of linearized hydrodynamics the complex frequency vanishes with wave vector at all temperatures, the question of how to take the limit of the complex frequency tending to zero is discussed briefly. Finally, we relate the preceding discussion to some concepts of Kohn and Sherington.[11]

Section IV is devoted to some examples of such soft modes, and also comments on the validity of the above discussion to first-order phase transitions.

II. STATIC RESPONSE AND STABILITY LIMIT

We shall now discuss in greater detail the concept of thermodynamic stability and its relation to the response of the system to a time-independent external field from the point of view of equilibrium statistical mechanics. Consider a many-body system in thermodynamic equilibrium and let us subject it to an external field $V_{\rm ext}(\vec{r})$, which couples to a local order parameter $\Psi(\vec{r})$. We may write for the Hamiltonian of the system

$$H = H_0 - \int V_{\rm ext}(\vec{r})\Psi(\vec{r})\,d\vec{r}\ . \tag{1}$$

An example of such a local order parameter is the local magnetization in a magnet; one refers to the external field which couples to it as the "conjugate ordering field." The static (isothermal) response function $\chi^T_{\Psi\Psi}$ may be defined as[12]

$$\left.\frac{\delta\langle\Psi(\vec{r})\rangle}{\delta V_{\rm ext}(\vec{r}')}\right|_T = \chi^T_{\Psi\Psi}(\vec{r},\ \vec{r}')\ , \tag{2}$$

where

$$\langle\Psi(\vec{r})\rangle = \mathrm{Tr}[\rho\Psi(\vec{r})]\ . \tag{3}$$

Here ρ is the full density matrix defined by

$$\rho = e^{-\beta H}/\mathrm{Tr}e^{-\beta H}\ , \tag{4}$$

with $\beta = 1/k_BT$. Provided that the external field is weak one can invoke the formalism of "linear response theory" to obtain for the static response[13]

$$\chi^T_{\Psi\Psi}(\vec{r},\ \vec{r}') = \int_0^\beta [\langle e^{\lambda H_0}\Psi(\vec{r}')e^{-\lambda H_0}\Psi(\vec{r})\rangle_0 - \langle\Psi(\vec{r}')\rangle_0\langle\Psi(\vec{r})\rangle_0]\,d\lambda\ , \tag{5}$$

where $\langle\Psi\rangle_0$ refers to an ensemble average with respect to the equilibrium density matrix, viz.,

$$\langle\Psi\rangle_0 = \mathrm{Tr}\,(\rho_0\Psi)\ ,\quad \rho_0 = e^{-\beta H_0}/\mathrm{Tr}e^{-\beta H_0}\ . \tag{6}$$

For classical systems or more generally, if the order parameter commutes with the unperturbed Hamiltonian H_0, Eq. (5) reduces to

$$\chi^T_{\Psi\Psi}(\vec{r},\ \vec{r}') = \beta g_{\Psi\Psi}(\vec{r},\ \vec{r}')\ , \tag{7}$$

where

$$g_{\Psi\Psi}(\vec{r},\ \vec{r}') = \langle[\Psi(\vec{r}) - \langle\Psi(\vec{r})\rangle_0][\Psi(\vec{r}') - \langle\Psi(\vec{r}')\rangle_0]\rangle_0 \tag{8}$$

is the "pair correlation function."

Let us now return to the discussion of the stability of the system. We observe that the free energy of the system under consideration can be written as[14]

$$F = F_s[\langle\Psi(\vec{r})\rangle] - \int V_{\rm ext}(\vec{r})\langle\Psi(\vec{r})\rangle\,d\vec{r}\ , \tag{9}$$

where F is a universal functional (independent of $V_{\rm ext}$) of the variational parameter $\langle\Psi(\vec{r})\rangle$. This means, in particular, that all those $\langle\Psi(\vec{r})\rangle$ have to be rejected which do not correspond to a local minimum of $F[\langle\Psi(\vec{r})\rangle]$.

Invoking the minimum property of the free energy in this (restricted) local sense and the convexity of F_s, we obtain

$$\delta F_s[\langle\Psi\rangle]/\delta\langle\Psi(r)\rangle\big|_{\rm eq} = V_{\rm ext}(\vec{r})\ , \tag{10}$$

$$\delta^2 F_s[\langle\Psi\rangle]/\delta\langle\Psi(\vec{r})\rangle\delta\langle\Psi(\vec{r}')\rangle\big|_{\rm eq} > 0\ . \tag{11}$$

Equation (11), which expresses the convexity of F_s, can be rewritten to read [see Eq. (2)]

$$\left.\frac{\delta^2 F_s}{\delta\langle\Psi(\vec{r})\rangle\delta\langle\Psi(\vec{r}')\rangle}\right|_{\rm eq} = [\chi^T_{\Psi\Psi}(\vec{r},\vec{r}')]^{-1} > 0\ . \tag{12}$$

This states that for equilibrium ensembles the static response of the system to a time-independent field must be positive. When the response function tends to be infinite the equilibrium state is no longer a stable state. At this point it is useful to introduce the corresponding functions in Fourier space. If we assume that in the absence of the external field the system is translationally invariant we can write

$$\chi^T_{\Psi\Psi}(\vec{Q}) = \int e^{i\vec{Q}\cdot(\vec{r}-\vec{r}')}\chi^T(\vec{r}-\vec{r}')\,d(\vec{r}-\vec{r}')$$

$$= \int_0^\beta d\lambda \, [\langle e^{\lambda H_0} \Psi(\vec{Q}) \, e^{-\lambda H_0} \Psi(-\vec{Q}) \rangle_0 - \langle \Psi(\vec{Q}) \rangle_0 \langle \Psi(-\vec{Q}) \rangle_0] \, . \quad (13)$$

For classical systems we have [Eq. (7)],

$$\chi^T(\vec{Q}) = \beta S(\vec{Q}) \, , \quad (14)$$

where $S(\vec{Q})$ is the familiar structure factor and is the Fourier transform of the pair correlation function $g(\vec{r} - \vec{r}')$ [Eq. (8)]. We now define the *stability limit* as

$$\chi^T_{\Psi\Psi}(\vec{Q}) = \infty \, . \quad (15)$$

When this limit is reached the system evolves to a new state with the new free energy a (local) minimum. If such a process occurs in the absence of any external field due to, say, a change of the parameters that determine the thermodynamic functions, then one speaks of a *phase transition*. At the stability limit $\chi(\vec{Q})$ may diverge at one or more wave vectors, which we shall call the critical wave vector $\vec{Q}_c$. The specific value (or values) of this critical wave vector will influence the symmetry properties of the new stable phase. An instability at $\vec{Q}_c = \vec{0}$ is associated with the divergent fluctuations of a macroscopic (long-wavelength) order parameter. Examples of such an instability are the paramagnetic-ferromagnetic transition and transitions at the critical point of fluids. An infinite response function at $\vec{Q}_c \neq \vec{0}$ is associated with microscopic order parameter fluctuations and the new stable phase will possess an order parameter of that wave vector. Examples of this are the paramagnetic-antiferromagnetic transition[7] and certain continuous structural phase transitions.[8,9] To summarize this section then, we have said that continuous equilibrium phase transitions may be investigated by studying the stability of the system with respect to an infinitesimal static external field. The system is unstable if the static response is negative. When the response is infinite it is said that the system has reached the stability limit and will evolve to a new equilibrium stable state.

III. DYNAMICAL RESPONSE AND SOFT MODES

We now turn to the dynamic response of the system. Let us perturb the system from its equilibrium by a time-dependent external field. When we switch off the field the system will relax back to equilibrium. As we shall soon see, this "approach to equilibrium" is related to excitation of normal modes of the system. Suppose, prior to the application of the field, the system is at the limit of stability against a continuous phase transition—as discussed previously. We would now like to relate this to the behavior of the dynamic response function.

We saw earlier that at the stability limit the static isothermal response function diverges. We should now like to see how the static response function is related to the above-mentioned dynamical response function. Intuitively one would be tempted to say that the static response function is simply the $\omega = 0$ Fourier component of the dynamical response function. This, however, is not generally true. This subtle question has been discussed by Kubo in his beautiful paper.[13] Since this identification plays a crucial role in the subsequent discussion it would serve well to bring out the underlying assumptions explicitly. We therefore give below a brief outline of Kubo's arguments.

Let us consider an isolated system in thermal equilibrium. Let it be described by a density matrix ρ_0 and a time-independent Hamiltonian H_0 which commutes with ρ_0. We shall assume that the system in this equilibrium phase is characterized by an order parameter $\Psi(\vec{r}, t)$.

Let us subject this system to a weak external field $V_{\text{ext}}(\vec{r}, t)$, which has been switched on adiabatically in the infinite past. Mathematically this may be written as

$$V_{\text{ext}} = \lim_{\epsilon \to 0+} V_{\text{ext}}(\vec{r}, t) e^{\epsilon t} \, . \quad (16)$$

It can be shown that, to first order in the external field, the change in the ensemble-averaged order parameter due to the departure of the system from its equilibrium phase, may be written as[13,15]

$$\delta\langle \Psi(\vec{r}, t) \rangle = \lim_{\epsilon \to 0+} \int d\vec{r}' \int_{-\infty}^{+\infty} dt' \, \tilde{\chi}(\vec{r}, \vec{r}'; t - t') \times V_{\text{ext}}(\vec{r}', t') e^{\epsilon t'} \, , \quad (17)$$

where

$$\tilde{\chi}(\vec{r}, \vec{r}'; t - t') = (i/\hbar) \langle [\Psi(\vec{r}', t'), \Psi(\vec{r}, t)] \rangle_0 \theta(t - t') \quad (18)$$

is defined as the retarded response function. Here the angular bracket corresponds to an average with respect to the equilibrium density matrix ρ_0, the square bracket corresponds to a commutator, and the unit step function $\theta(t - t')$ expresses the retarded or causal nature of the response. For the sake of simplicity let us consider a monochromatic external disturbance, viz.,

$$V_{\text{ext}} = \lim_{\epsilon \to 0+} \tfrac{1}{2} [V_{\text{ext}}(\vec{Q}, \omega) e^{-i(\vec{Q} \cdot \vec{r} - \omega t)} + \text{c.c.}] e^{\epsilon t} \, . \quad (19)$$

With this choice Eq. (17) now reads

$$\delta\langle \Psi(\vec{r}, t) \rangle = \tfrac{1}{2} [\chi_{\Psi\Psi}(\vec{Q}, \omega) V_{\text{ext}}(\vec{Q}, \omega) \times e^{-i(\vec{Q} \cdot \vec{r} - \omega t)} + \text{c.c.}] \, e^{\epsilon t} \, , \quad (20)$$

where $\chi_{\Psi\Psi}(\vec{Q}, \omega)$ is the complex response function and is the Fourier transform of $\tilde{\chi}(\vec{r} - \vec{r}'; t - t')$, viz.,

$$\chi_{\Psi\Psi}(\vec{Q},\ \omega)=\lim_{\epsilon\to 0+}\int_{-\infty}^{+\infty} d(t-t')\int d(\vec{r}-\vec{r}')\tilde{\chi}(\vec{r}-\vec{r}';\ t-t')\exp[-i\vec{Q}\cdot(\vec{r}-\vec{r}')-i\omega(t-t')]\exp[-\epsilon(t-t')] \quad (21)$$

$$=\lim_{\epsilon\to 0+}\left(\frac{i}{\hbar}\right)\int_0^{\infty} dt\, e^{-i\omega t-\epsilon t}\langle[\Psi(\vec{Q},\ t),\ \Psi(-\vec{Q},\ 0)]\rangle_0 \ . \quad (22)$$

In writing Eq. (21) we have assumed that the system is translationally invariant. Further, since the time integral in Eq. (22) goes only from 0 to ∞ we may "redefine" the response function as

$$\tilde{\chi}(\vec{Q},t)=(i/\hbar)\,\mathrm{Tr}\{\rho_0[\Psi(\vec{Q},t),\Psi(-\vec{Q},0)]\} \quad (23)$$

$$=(i/\hbar)\,\mathrm{Tr}\{[\rho_0,\ \Psi(-\vec{Q},0)]\Psi(\vec{Q},t)\}$$

$$=-\int_0^{\beta} d\lambda\,\mathrm{Tr}\{\rho_0 e^{\lambda H_0}\Psi(-\vec{Q},0)\,e^{-\lambda H_0}\dot{\Psi}(\vec{Q},t)\}\ , \quad (24)$$

where $\dot{\Psi}(t)$ is the time derivative evaluated at time t. Substituting (24) into (22), and after partial integration one obtains

$$\chi_{\Psi\Psi}(\vec{Q},\ \omega)=R_{\Psi\Psi}(\vec{Q},\ t=0)-i\omega\int_0^{\infty} R_{\Psi\Psi}(\vec{Q},\ t)e^{-i\omega t}\,dt \ . \quad (25)$$

$R_{\Psi\Psi}(\vec{Q},\ t)$ is defined by

$$R_{\Psi\Psi}(\vec{Q},\ t)=\lim_{\epsilon\to 0+}\int_t^{\infty}\tilde{\chi}(\vec{Q},\ t')e^{-\epsilon t'}\,dt' \quad (26)$$

and is called the *relaxation function*. Explicit integration of (26) yields

$$R_{\Psi\Psi}(\vec{Q},\ t)=\int_0^{\beta} d\lambda\,\mathrm{Tr}\{\rho_0 e^{\lambda H_0}\Psi(-\vec{Q},0)\,e^{-\lambda H_0}\Psi(\vec{Q},t)\}$$

$$-\lim_{t\to\infty}\int_0^{\beta} d\lambda\,\mathrm{Tr}\{\rho_0 e^{\lambda H_0}\Psi(-\vec{Q},0)\,e^{-\lambda H_0}\Psi(\vec{Q},t)\}\ . \quad (27)$$

Kubo has argued that the limit of the second term in the above equation, if it exists, must be equal to

$$-\beta\,\mathrm{Tr}[\rho_0\bar{\Psi}(\vec{Q})\bar{\Psi}(-\vec{Q})]\ , \quad (28)$$

where $\bar{\Psi}$ is the diagonal part of Ψ with respect to H_0.

Returning to Eq. (25) we see at once that

$$\chi_{\Psi\Psi}(\vec{Q},\ \omega=0)=R_{\Psi\Psi}(\vec{Q},\ t=0)\ . \quad (29)$$

Comparing Eqs. (27) and (13) we see that

$$\chi_{\Psi\Psi}(\omega=0)\neq\chi^T_{\Psi\Psi}$$

unless

$$\mathrm{Tr}[\rho_0\bar{\Psi}(\vec{Q})\bar{\Psi}(-\vec{Q})]=\mathrm{Tr}[\rho_0\Psi(\vec{Q})]\,\mathrm{Tr}[\rho_0\Psi(-\vec{Q})]\ . \quad (30)$$

$\chi_{\Psi\Psi}(\omega=0)$ is the static response of an isolated system on which an external perturbation is switched on adiabatically. $\chi^T_{\Psi\Psi}$ as given by Eq. (2) is the isothermal response of a system. These, in general, need not be equal. However, they *are* identical if one assumes that the order parameter is an ergodic variable. For classical systems the assumption of ergodicity reads as follows:

$$\langle\Psi\rangle=\lim_{t\to\infty}\frac{1}{t}\int_0^t\Psi(t')\,dt' \ . \quad (31)$$

There are situations where this ergodicity assumption cannot be made. Kubo[13] has argued that one can expect that

$$\chi_{\Psi\Psi}(\omega=0)=\chi^T_{\Psi\Psi} \quad (32)$$

will hold if the total system is large enough compared to the degrees of freedom associated with the observable Ψ.

To summarize what we have said until now: If one assumes the ergodicity of the order parameter then *the* $\omega=0$ *Fourier component of the dynamical response function* $\chi_{\Psi\Psi}(\omega)$ *is just the static isothermal response function* $\chi^T_{\Psi\Psi}$. We may therefore write the limit of stability against an equilibrium phase transition as

$$\chi^T_{\Psi\Psi}(\vec{Q})=\chi_{\Psi\Psi}(\vec{Q},\ \omega=0)=\infty \ . \quad (33)$$

We now turn to a discussion of the excitation spectrum of the many-body system. It is well known that *stable* collective excitations of the many-body equilibrium state correspond to poles in the lower half of the complex frequency plane of the dynamical response function $\chi_{\Psi\Psi}(\vec{Q},\ \omega)$. At this point it would be worthwhile recalling some of the analytic properties of the response function. This function, defined in (21) for real ω, can be analytically extended everywhere in the complex frequency plane (z plane). Such a function $\chi_{\Psi\Psi}(\vec{Q},\ z)$ is separately analytic everywhere in the upper and lower half-planes and has a branch cut along the real axis (see Fig. 1). An immediate consequence of this branch cut is the fact that along it

$$\chi_{\mathrm{I}}-\chi_{\mathrm{II}}=2i\,\mathrm{Im}\chi_{\mathrm{I}} \ . \quad (34)$$

Even though χ_{II} is analytic in the lower half of the z plane, the analytic continuation of χ_{I} into the lower half-plane (defined as $\chi_{\mathrm{I}C}$) is no longer analytic there. In fact, the analytic continuation must have the same analytic properties as the difference $(\chi_{\mathrm{I}}-\chi_{\mathrm{II}})$, i.e., as the function $\mathrm{Im}\chi_{\mathrm{I}}(z)$. The poles of $\chi_{\mathrm{I}C}(z)$, if there are any, are the collective modes of the system. Here we make the following parenthetical comment: One cannot say *a priori* whether $\chi_{\mathrm{I}C}(z)$ will have poles. In fact one can enunciate mathematical models which are completely devoid of dynamics, and consequently $\chi_{\mathrm{I}C}(z)$ will have no

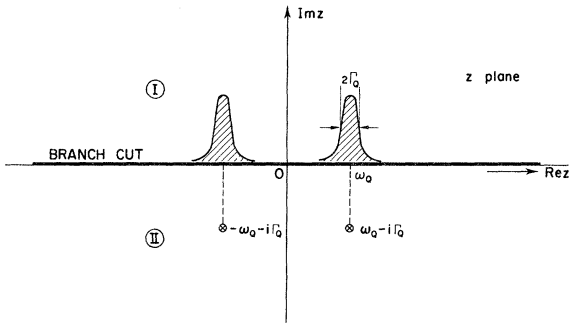

FIG. 1. We have displayed the branch cut of the function $\chi_{\Psi\Psi}(\vec{Q}, z)$. It is separately analytic in the regions I and II. For the purpose of illustration we have shown two typical poles of the function $S(\vec{Q}, \omega)$. In an experiment such a complex pole would show up as a broadened peak.

poles. In what follows we exclude from our discussion such systems and only treat realistic physical systems where one would expect to have collective modes. Let these correspond to a set of discrete poles at $z_i = \omega_i(\vec{Q}) - i\Gamma_i(\vec{Q})$. At these singular points $\chi_{IC}(\vec{Q}, z_i)$ will diverge. We know, however, that as the system evolves towards the stability limit, we must have

$$\chi_{\Psi\Psi}(\vec{Q}, z=0) \to \infty \tag{35}$$

[see Eq. (33)].

We shall now examine whether the behavior of $\chi(\vec{Q}, z)$ *at* $z=0$ is related to the singularity structure of $\chi(\vec{Q}, z)$ in the lower half-plane. Specifically, we shall endeavor to show that the divergence of $\chi(z)$ at the origin is due to one of the poles of $\chi(\vec{Q}, z)$ in the lower half-plane moving to the origin; i.e., one of the collective modes becoming "soft."

Let us first recall that[4]

$$\chi(\vec{Q}, z=0) = P\int_{-\infty}^{+\infty} \frac{d\omega}{\pi} \frac{\chi''(\omega)}{\omega} , \tag{36}$$

where P refers to a principal value integral and $\chi''(\omega) = \mathrm{Im}\chi(\omega)$. Therefore, as we approach the stability limit the area under $\chi''(\omega)/\omega$ diverges. Next, let us consider the first frequency moment of $\chi''(\omega)$, viz.,

$$\int_{-\infty}^{+\infty} \chi''(\omega)\, \omega\, d\omega . \tag{37}$$

From the definition of the response function it follows that[15]

$$\int_{-\infty}^{+\infty} \frac{d\omega}{2\pi}\, \omega\, \chi''_{\Psi\Psi}(Q, \omega) = i \left\langle \left[\frac{\partial \Psi(\vec{Q}, t)}{\partial t} , \Psi(-\vec{Q}, 0) \right] \right\rangle_0$$

$$= \langle [[\Psi(\vec{Q}), H_0], \Psi(-\vec{Q})] \rangle_0 . \tag{38}$$

The existence of this moment is related to "local conservation laws" of the form[16]

$$\frac{\partial \Psi(Q)}{\partial t} + i\vec{Q} \cdot \vec{J}^{\Psi}(\vec{Q}) = 0 , \tag{39}$$

where $\vec{J}^{\Psi}(\vec{Q})$ is the "current" associated with the operator $\Psi(\vec{Q})$. When $\Psi(\vec{Q})$ is the particle density $\rho(\vec{Q})$, for example, the relevant conservation law is that of particle number, and the first moment [Eq. (38)] is just the famous f sum rule.[4] The important observation for us is that one believes that in any equilibrium phase the first moment of $\chi''(\vec{Q}, \omega)$ exists, and is finite. Let us now follow the system as it evolves towards the stability limit. The only way by which the area under $\chi''(\vec{Q}, \omega)/\omega$ can diverge, but the area under $\omega^2[\chi''(\vec{Q}, \omega)/\omega]$ remains finite, is if the main contribution to the integral [Eqs. (36) and (37)] comes from small ω, i.e., $\chi''(\vec{Q}, \omega)/\omega$ is peaked for small ω. This can be given a direct interpretation in terms of the behavior of the collective modes. In order to do this we introduce the dynamic form factor $S(Q, \omega)$ which is related to $\chi''(Q, \omega)$ through the fluctuation-dissipation theorem

$$S_{\Psi\Psi}(\vec{Q}, \omega) = (\hbar/\pi)[1 - e^{-\beta\hbar\omega}]^{-1} \chi''_{\Psi\Psi}(\vec{Q}, \omega) . \tag{40}$$

The dynamic form factor $S(\vec{Q}, \omega)$ is just the density of states with energy $\omega > 0$ and momentum $\vec{Q}$, which are excited by the probe which couples to Ψ. If $\beta\omega \ll 1$, $\omega, \beta^{-1} > 0$, this density of states may be approximated by

$$S_{\Psi\Psi}(\vec{Q}, \omega) \approx (1/\pi\beta\omega)\chi''_{\Psi\Psi}(\vec{Q}, \omega) . \tag{41}$$

Alternatively, $\chi''_{\Psi\Psi}(\vec{Q}, \omega)/\beta\omega$ may be interpreted as the density of low-lying states excited by the probe. Keeping this in mind we can define a mean-square excitation energy as

$$\omega^2_{\mathrm{av}} = \int_0^{\infty} \frac{d\omega}{2\pi}\, \omega^2\, \frac{\chi''(\omega)}{\omega} \Big/ P\int_0^{\infty} \frac{d\omega}{2\pi} \frac{\chi''(\omega)}{\omega} . \tag{42}$$

As we approach the transition the denominator gets very large, the numerator, of course, is a finite constant for fixed $\vec{Q}$, so that ω^2_{av} becomes smaller and smaller and tends to zero at the stability limit.

The above arguments clearly show that the divergence of $\chi_{\Psi\Psi}(\vec{Q}, z)$ at $z=0$, at the stability limit, is related to the excitation spectrum of Ψ. It *rules out*, for example, the possibility that $\chi(\vec{Q}, z=0)$ diverges as a function of some thermodynamic parameter but leaves the excitation spectrum unaffected. So far we have discussed the behavior of the system in terms of the real function $S(\vec{Q}, \omega)$ that one measures, say, in a scattering experiment. Let us for a moment revert to the complex response function $\chi_{\Psi\Psi}(\vec{Q}, z)$. As already remarked upon, when the system is *stable* all the singularities of $\chi_{\Psi\Psi}(\vec{Q}, z)$ are in the lower half-plane. On the basis of what has been stated above one can now assert that approaching a phase transition at least one of the poles of $\chi(\vec{Q}, z)$ in the lower half-plane moves to the origin and, consequently, $\chi(\vec{Q}, z=0)$

diverges. In other words, one of the collective modes becomes *soft*—the complex frequency of the mode goes to zero. The following point should be emphasized in this context. It is well known, in linearized hydrodynamics for example, that the complex frequency of certain modes goes to zero with the *wave vector* at all temperatures. The existence of such "gapless" excitations follows from Goldstone's theorem.[16] We do not refer to such a vanishing of the frequency as the softening of the mode. We say that a mode becomes soft if its complex frequency vanishes, at a finite wave vector, due to changes in the thermodynamic parameters of the system. If one were observing these modes in a scattering experiment, say, the following would be observed: In a scattering experiment one measures the dynamical form factor $S(\vec{Q}, \omega)$ which is related to the $\mathrm{Im}\chi_I(\vec{Q}, \omega)$ through the celebrated fluctuation-dissipation theorem.[4] Away from the stability limit the "real function" $S(\vec{Q}, \omega)$ will have broad peaks centered around $\{\omega_i(\vec{Q})\}$ (see Fig. 1). What we have argued above implies that as the system approaches the stability limit at least one of these peaks must move towards $\omega = 0$, and the half-width of the peak must tend to zero. In the special case when $\vec{Q}_c = 0$ the critical modes represent the modes of linearized hydrodynamics. Their frequencies will be related to purely thermodynamic quantities, whereas their decay rates will be related to thermodynamic quantities and transport coefficients.[10] As mentioned above, in this special case care must be taken to go to the limit $\omega \to 0$.

We shall now attempt to relate the preceding discussion to an interesting idea due to Kohn and his collaborators.[11] For our purpose it is necessary to recapitulate some of the salient features of their arguments. Kohn *et al.* have argued that there are two kinds of bosons: Bosons of type I are complexes of even numbers of fermions (or fermion holes)—e.g., ^{4}He atoms. Bosons of type II are bound complexes of equal numbers of fermions and their holes. Examples of these are "collective excitations" like excitons, phonons, magnons, etc. They have argued that certain classes of phase transitions may be viewed as due to the formation of type-II condensate. They suggest that many distortive transitions may be viewed as the condensation of soft phonons.

We have argued that the divergence of the static susceptibility at the stability limit, and the finiteness of the second moment of $\chi''_{\Psi\Psi}(\vec{Q}, \omega)/\omega$ arbitrarily close to the instability, imply that the density of excited states is peaked near the origin at the instability. This implies that the zero-frequency excitation, namely, the soft mode, is predominantly excited. Alternatively, one can say that the system condenses into this soft mode. It should be noted that it is in this sense that Kohn *et al.* use the word "condensate of type II."

III. EXAMPLES OF SOFT MODES

A. Continuous Phase Transitions

Let us briefly recall what we have so far stated. Following Landau we have said that a thermodynamic phase in equilibrium can be characterized by an order parameter and that the free energy is a minimum considered as a function of this order parameter. At the limit of stability the second variation of the free energy is zero and this corresponds to an infinite order parameter–order parameter response function. We have proved in Sec. III that at this limit of stability there must occur at least one soft mode. Now, it is believed that equilibrium phase transitions occur on the coexistence curve. The critical point (or line) is the coincidence of the stability limit and the coexistence curve. Phase transitions which occur at the critical point should, according to our arguments, exhibit soft modes. We now give several examples.

1. *Ferroelectric Transition*

As a first example let us discuss the ferroelectric order-disorder transition in KH_2PO_4. In this crystal, each proton has two equilibrium positions along its bond, close to one or the other of its PO_4 neighbors. At $T > T_c$ both of these positions are occupied, but at low temperature the proton system goes over into an ordered configuration. According to Cochran's theory[6] this transition is associated with an infrared-active mode which becomes soft and which is responsible for the blowing up of the dielectric constant. The order parameter is here obviously the polarization. The soft-mode picture has been substantiated for example in the experiments of Kaminov and Damen.[17]

2. *Structural Transitions*

$SrTiO_3$ is a good example of a structural transition which is believed to be of second order. The nature of the transition is as follows: below T_c the BO_6 octahedra are rotated with respect to the cube axes, with the sense of rotation alternating from cell to cell in all three directions. Consequently the mean value of the rotation angle is the order parameter. This picture has emerged, for example, in electron paramagnetic resonance (EPR) measurements.[2] Neutron measurements have revealed that an optic mode at the R corner of the Brillouin zone becomes soft.[18]

3. λ *Transition of* ^{4}He *and Transition to Superconducting State*

Here the order parameter is the complex condensate wave function, $[n_0(\vec{r})]^{1/2}e^{i\varphi}$, where $n_0(\vec{r})$ is the local number of He atoms in the condensate or the

local number of Cooper pairs of electrons in a superconductor. The phase φ defines the superfluid velocity according to $v_s = -(\hbar/m^*)\nabla\varphi$, where m^* is the atomic mass in He and twice the electronic mass in superconductors. The motion of the superfluid component may then be different from that of the normal component, and this gives rise to a new mode of excitation, the second sound, both in superfluid ^{4}He and in the superfluid electron fluid in the superconductor. In both cases the second-sound velocity goes to zero when T_c is approached from below and becomes a thermal diffusion mode above T_c, i.e., there is no second sound in the normal phase of ^{4}He or of metals. In the latter case the second-sound mode below T_c is overdamped because of electron-lattice interaction (an overdamped second sound in the combined electron-phonon system may occur above T_c).[19] Hence second sound is the soft mode of superfluid ^{4}He[20] and of superconductors for $T \to T_c^-$ and an overdamped mode for $T \to T_c^+$. Clearly these transitions are macroscopic ones and therefore $Q_c = 0$.

4. *Liquid-Gas Transition*

As already mentioned, the liquid-gas density difference $(\rho_L - \rho_G)$ is the order parameter, because it is nonzero only in the ordered phase. Brillouin scattering experiments have shown[21] that the thermal diffusion mode with purely imaginary frequency is here the soft mode with wave number $\vec{Q}_c = \vec{0}$.

B. Discontinuous Phase Transitions

It is a fact of experience that discontinuous (first-order) transitions occur even before the system reaches its stability limit. More precisely it is believed that the transition occurs on the coexistence curve of the two phases where the chemical potentials of the two phases are equal. In certain theoretical models, such as van der Waals's theory, the stability limit occurs at the end point of its "metastable" state.[22] The actual occurrence of such metastable states in any *exact* theory is presently a matter of controversy. In real systems, however, one expects that even as the system approaches the coexistence curve it must exhibit precursors of the new state. In this sense, we anticipate that physical properties which exhibit anomalous behavior at the stability limit proper would already begin to exhibit this tendency even as the system evolves to the coexistence curve. For example, the softening of a mode, which would have become unstable had we been able to take the system to the stability limit, should already be detectable. We now give a few examples of this.

1. *Ferroelectric Transitions*

$BaTiO_3$,[23] $PbTiO_3$,[24] SbSI,[25] and $Pb_{1-x}Ba_xTiO_3$[26,27] are good examples of ferroelectric transitions which are of first order. The order parameter in these transitions is the polarization. The soft mode is an infrared-active mode (with $\vec{Q}_c = \vec{0}$) and its frequency tends to zero. However, as one would expect on the basis of the remarks made above, the transition occurs before the frequency of the mode actually vanishes.

2. *Structural Phase Transition*

The α-β transition in quartz is a first-order transition. This is supported by Brillouin scattering[28] experiments and by the observation[29] of the coexistence of the two phases around 573 °C. The rotation angle of the SiO_4 tetrahedra about their respective twofold axis may here be treated as an approximate order parameter.[30] The soft made associated with this transition has been identified as a Raman-active mode at the center of the Brillouin zone, but the frequency of the mode remains finite at the transition temperature.[30]

3. *Liquid-Solid Transition*

It has been recently shown[31,32] that the "critical" density fluctuations of wave vector $\vec{Q}_0 (= \vec{Q}_c)$ in the liquid may be considered as the precursors of the new phase—the solid phase. $\vec{Q}_0$ is the position of the first peak of the structure factor $S(\vec{Q})$ and corresponds to the first reciprocal-lattice vector of the structure into which the liquid crystallizes. The associated soft mode is related to density-density correlations, and is of the type known as "relaxation mode" (purely imaginary frequency with wave number Q_0). Associated with this soft mode is a pressure-dependent or a temperature-dependent narrowing of the quasielastic peak in the dynamic form factor $S(\vec{Q}_0, \omega)$.

4. *Superfluid-Solid Transition of* ^{4}He

In analogy to classical liquids one expects "critical" density fluctuations of wave number $Q_c = Q_0$ in the pressure-induced superfluid-solid transition of ^{4}He of $T = 0$ °K. Q_0 is again the position of the first maximum in the structure factor $S(Q)$ and corresponds to the first reciprocal-lattice vector into which the liquid crystallizes. The associated soft mode has recently been suggested to be the roton minimum with frequency $\omega(Q_0)$.[33] This prediction is consistent with the observed pressure dependence both of the roton minimum[34] and of the first maximum of the structure factor at Q_0.[35]

5. *Antiferromagnet–Spin-Flop State Transition*

The phase transition of a uniaxial antiferromagnet into the spin-flop state is of first order. Blazey *et al.*[36] have shown that in a cylindrical sample of $GdAlO_3$ with easy axis and the applied field parallel to the cylindrical axis, the frequency of the antiferromagnetic resonance mode extrapolates to zero

at the stability limit of the antiferromagnetic phase. This softening has further been substantiated[37] by changing the temperature and therefore the stability limit of the antiferromagnetic phase; at each temperature the soft-mode frequency extrapolates to zero at the appropriate stability limit. In particular, by approaching the triple point the metastable region shrinks[38] and the mentioned soft-mode frequency vanishes at the actual transition, which is now of second order.

V. SUMMARY AND DISCUSSION

There are numerous characterizations of equilibrium phases and transitions between them. From the point of view of equilibrium thermodynamics a state in thermal equilibrium corresponds to one of maximum entropy. One further requires that the free energy of the equilibrium phase, considered as a function of a suitable "order parameter," be a minimum. These two statements are equivalent to the assertion that the specific heat and the order parameter–order parameter response function be positive. The choice of the order parameter for a given phase change of the system may or may not be unique. One may test for the stability of an equilibrium state by observing its response to a suitable static external field. An infinite response signals an unstable state.

From a microscopic point of view one may examine the stability problem in terms of the stability of the "collective excitations" of the many-body system. This is done, in the linear response regime, by observing the approach to equilibrium of the system when we perturb it with an infinitesimal time-dependent external field. We have argued in Sec. III that when the equilibrium state is at the limit of stability then it must be unstable with respect to the excitation of at least one of the collective modes. Another way of saying this is that at least one of the collective modes must go soft, i.e., its complex frequency goes to zero as the system evolves towards the stability limit. In proving this result we have made the following assumptions:

(a) In testing the stability of the system against an external perturbation we have assumed that the response is linear.

(b) We have assumed that the order parameter is an ergodic variable of the system. This was done to relate the static isothermal response to $\chi_{\Psi\Psi}(\vec{Q},\ \omega=0)$.

(c) We have restricted ourselves to systems with dynamics. More specifically, we have assumed that $\chi_{IC}(z)$ has poles in the lower half-plane.

(d) We have assumed that the second frequency moment of $\chi''_{\Psi\Psi}(\vec{Q},\omega)/\omega$ exists as long as the system is stable.

Assumption (a) is a reasonable one if a spontaneous phase change occurs at the stability limit of the system. This, for example, is the case for phase transitions at the critical point. However, at a first-order transition that occurs on the coexistence curve the system is, in fact, stable with respect to an infinitesimal perturbation. The assumption that the order parameter is an ergodic variable is nontrivial. In an *ideal* magnet, for example, the isothermal and adiabatic susceptibilities are not equal. In realistic systems with various interactions one would expect the difference between the two susceptibilities to be small.[13] In certain systems the second moment of $\chi_{\Psi\Psi}(\vec{Q},\omega)/\omega$ has been rigorously evaluated, for example, for density fluctuations in solids and liquids[4] and spin-density fluctuations in ferromagnets and antiferromagnets,[7] and is found to be finite. Since in these instances the existence of this moment is a requirement that the theory be invariant with respect to gauge transformations of the first kind one may anticipate that this would also be the case for systems with other order parameters.

We have also suggested, following Kohn and coworkers, that certain classes of phase transitions may be viewed as a Bose condensation of the soft mode. In this connection the following point should be made: In any given transition, say between phases I and II, the same physical quantity might be responsible for the instability when we go from phase I to phase II as when we go from phase II to phase I. However, the macroscopic manifestation of the mode that goes soft might be different. For example, the soft mode might be a propagating mode in one phase and a diffusive type in the other. This is the case in the λ transition in ^{4}He.[10] All that the above analysis can say is that at least one of the poles of the lower half of the complex frequency plane of the order parameter correlation function must move to the origin. To make a detailed assignment as to which collective mode goes soft one would have to examine the detailed behavior of $\chi_{\Psi\Psi}(\vec{Q},\ \omega)$ in each instance.

All of the preceding discussion has singled out the order parameter–order parameter response function. There may however be various other operators of the system whose correlation lengths also diverge, perhaps less strongly, at the stability limit. The divergence of the specific heat which expresses the divergence of the energy-energy correlation length, for example, is always weaker than the divergence of the susceptibility. It must be borne in mind that associated with every singular correlation function there must be a soft mode (our analysis of Sec. III is equally applicable to other correlation functions). Finally, it has been demonstrated that if the critical mode is a hydrodynamic mode ($Q_c=0$) then its excitation energy and its half-width may be described in terms of "critical exponents" of thermodynamic derivatives and of trans-

port coefficients.[10]

ACKNOWLEDGMENTS

We wish to acknowledge discussions with M. E. Fisher, G. B. Benedek, F. Shimizu, H. Thomas, E. Pytte, K. A. Müller, E. Stoll, H. Rohrer, and U. T. Höchli.

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[1]L. D. Landau and E. M. Lifshits, *Statistical Physics* (Addison-Wesley, Reading, Mass., 1958), Sec. 135.

[2]See, for example, K. A. Müller, W. Berlinger, and F. Waldner, Phys. Rev. Letters 25, 273 (1968).

[3]For example, the spontaneous magnetization M_s is determined from the condition that $(\partial F/\partial M)|_T = 0$.

[4]D. Pines and P. Nozières, *The Theory of Quantum Liquids* (Benjamin, New York, 1966), Chap. 2.

[5]H. Thomas, IEEE Trans. Magnetics Mag-5, 874 (1969).

[6]W. Cochran, Advan. Phys. 9, 387 (1960); 10, 401 (1961).

[7]W. Marshall and R. D. Lowde, Rep. Progr. Phys. 31, 705 (1968).

[8]J. M. Worlock, in Proceedings of the Geilo Conference on Structural Phase Transitions and Soft Modes (unpublished).

[9]G. Shirane, in Proceedings of the Geilo Conference on Structural Phase Transitions and Soft Modes (unpublished).

[10]P. C. Hohenberg, in *Critical Phenomena, Proceedings of the International School of Physics "Enrico Fermi"*, edited by C. Domb (Academic, New York, to be published).

[11]W. Kohn and D. Sherrington, Rev. Mod. Phys. 42, 1 (1970), and the references cited therein.

[12]See, for example, M. H. Cohen, Phys. Rev. 130, 1301 (1963).

[13]K. Kubo, J. Phys. Soc. Japan 12, 570 (1957).

[14]P. C. Hohenberg and W. Kohn, Phys. Rev. 136, B864 (1964); N. D. Mermin, *ibid.* 137, A1441 (1965).

[15]P. C. Martin, in *Many Body Physics*, edited by C. De Witt and R. Balian (Gordon and Breach, New York, 1967).

[16]H. Wagner, Z. Physik 195, 273 (1966).

[17]I. P. Kaminow and T. C. Damen, Phys. Rev. Letters 20, 1105 (1968).

[18]G. Shirane and Y. Yamada, Phys. Rev. 177, 858 (1969).

[19]C. P. Enz (unpublished).

[20]See, for example, J. Wilks, *Liquid and Solid Helium* (Clarendon, Oxford, 1967), p. 71.

[21]H. L. Swinney and H. C. Cummins, Phys. Rev. 171, 152 (1968).

[22]See Ref. 1, Chap. 8.

[23]G. Shirane, B. C. Frazer, V. J. Minkeiwicz, J. A. Leake, and A. Linz, Phys. Rev. Letters 19, 234 (1967).

[24]G. Burns and B. Y. Scott, Phys. Rev. Letters 25, 1191 (1970).

[25]E. F. Steigmeier, G. Harbeke, and R. K. Wehner (unpublished).

[26]G. Burns and B. A. Scott, Bull. Am. Phys. Soc. 16, 415 (1971).

[27]G. Burns and B. A. Scott (unpublished).

[28]S. M. Shapiro and H. Z. Cummins, Phys. Rev. Letters 21, 1578 (1968).

[29]U. T. Höchli, Solid State Commun. 8, 1487 (1970).

[30]U. T. Höchli, Phys. Rev. Letters 26, 1267 (1971).

[31]T. Schneider, R. Brout, H. Thomas, and J. Feder, Phys. Rev. Letters 25, 1423 (1970).

[32]T. Schneider, Phys. Rev. A 3, 2145 (1971).

[33]T. Schneider and C. P. Enz, Phys. Rev. Letters 27, 1186 (1971).

[34]D. G. Henshaw and A. D. B. Woods, *Proceedings of the Seventh International Conference on Low-Temperature Physics* (North-Holland, Amsterdam, 1961), p. 539.

[35]See Ref. 20, p. 286.

[36]K. W. Blazey, K. A. Müller, M. Ondris, and H. Rohrer, Phys. Rev. Letters 24, 105 (1970).

[37]H. Rohrer (private communication).

[38]K. W. Blazey, H. Rohrer, and R. Webster, Phys. Rev. B 4, 2287 (1971).